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## **Removal of radioactive Cs from gravel conglomerate using water containing air bubbles**

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### **Abstract**

Remediation of sites contaminated with radioactive material such as Cs is important because of the risk posed to human health. Here, we report the effectiveness of water containing air bubbles with a diameter around 100 nm (nanobubbled water, NB water) for the removal of radioactive Cs. Laboratory experiments confirmed that NB water is more effective than purified water and as effective as water with neutral detergent in the removal of Cs-137 from gravel. Moreover, NB water retains its effectiveness even after storage for 7 days. Finally, NB water produced onsite from tap water was found to be effective for removal of radioactive Cs from gravel conglomerate in Fukushima, Japan.

**Keywords:** Microbubble, nanobubble, removal of Cs, remediation, Fukushima crisis

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## 1. Introduction

The Fukushima Daiichi Nuclear Power Station suffered a meltdown as a result of the Tohoku earthquake of March 11, 2011, in Japan. The accident released several kinds of radioactive elements over eastern Japan. It is well known that I-131, Cs-134, and Cs-137 are the main radioactive elements that pose a risk of human exposure (IAEA report 2006). Among these, Cs-134 and Cs-137 are the most important in terms of their effects on the environment because the half-life of I-131 is relatively short and other kinds of radioactive elements such as Pu-239 cannot spread far from the nuclear reactor (Eisenbud 1973). Therefore, removal of Cs-134 and Cs-137 from the environment is very important for protecting human health.

Fallout Cs is stabilized in soil by ion exchange with alkali ions and is well known to be difficult to remove (Raskin & Ensley 1999, Willey 2007). Indeed, previous studies employing phytoremediation have failed to remove radioactive Cs from the soil (Willey 2007). Furthermore, although another trial using strong acid and/or chemicals was successful, such chemicals may themselves be environmental pollutants because they alter the pH of soils and the composition of inorganic ions, which strongly influence plant and animal growth. Thus, a more benign approach to remediation is required.

Here, we propose the use of nanobubbled (NB) water, that is, water containing air

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bubbles with a diameter of less than 100 nm. Although the characteristics of such water are not completely understood (Takahashi et al., 2002, Takahashi 2005, Takahashi et al., 2007, Agarwal et al., 2011), it is currently used on Japanese highways to remove de-icing salts (Yamazaki 2010) and in semiconductor plant to remove oil (Miyamoto & Ueyama). Additionally, NB water can be expected to be environmentally safe because it is identical to regular water.

The purpose of this study is to clarify the effectiveness of NB water in the removal of radioactive Cs from gravel conglomerate in the laboratory and in an on-site removal demonstration with radioactive material at Fukushima, Japan, using tap water.

## 2. Experimental

### 2.1 Preparation and characterization of NB water

NB water was generated by the centrifugal gas–liquid separation method (BUVITAS HYK-32-D, KYOWA KISETSU). As listed in Table 1, 50 L of purified water at a flow rate of 45 L/min and air at a rate of 0.7 L/min were subject to centrifugal rotation for 90 min to afford NB water. The NB water was used in pristine form (NB water P) and after storage for 16 h (NB water 16 h) or 7 days (NB water 7 d). Purified water was also examined for comparison.

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The size distribution of air bubbles in purified water and NB water was characterized using a laser-illuminated optical microscopic technique based on particle-tracking analysis (NANOSIGHT LM-10, Quantum Design, Inc.) (Gallego-Urrea et al. 2011). The detection limit was from 50 nm to 1000 nm depending on the particles and solvent.

*2.2 Removal of radioactive Cs from gravel conglomerates*

Gravel conglomerates were collected from the Fukushima Agricultural Technology Centre (FATC), Koriyama City, Fukushima Prefecture, Japan. In order to reduce the experimental error, the dried gravel conglomerates were pre-washed with purified water to remove the clay and then dried in a vacuum oven. The washing procedure was as follows: Mixtures comprising 100 g of dried gravel conglomerates with 100 mL of purified water or NB water were shaken at 160 rpm for 3 h. The gravel conglomerates were then separated from the water and then dried over 24 h in a vacuum oven.

The radiation intensity of the gravel conglomerates before and after washing with water and that of supernatant water was examined using a germanium semiconductor detector (GMX-18200-S, EG&G ORTEC). The detector was equipped with a 0.5-mm-thick Be window and its energy resolution at 5.9 keV was 0.54 keV. The radioactivity of the samples was estimated at 661 keV, which is the energy level specific to Cs-137. The

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removal ratio of Cs-137 was calculated as the average over three samples. In this study, only the removal ratio of Cs-137 was estimated because the abundance ratio of Cs-137 to Cs-134 is expected to be constant.

*2.3 On-site removal of radioactive Cs at Fukushima using tap water*

On-site washing with NB water was also performed for gravel conglomerate at FATC. NB water was produced using tap water at Fukushima under the same conditions as described previously.

Gravel conglomerates were collected at Fukushima and used without any pre-washing. Mixtures comprising 100 g of dried gravel conglomerates with 500 mL of purified water or NB water were kept in the room temperature without shaking for 12 h. The gravel conglomerates were then dried overnight. Mixtures comprising 500 g of dried gravel conglomerates with 1 L of purified water or NB water were also used. For comparative study, the washing procedures were also performed with 0.15 wt% of commercially-available neutral detergent added to purified water and NB water.

**3. Results and discussion***3.1 Size distribution of air bubbles in NB water*

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As shown in Fig. 1 and Table 1, the air bubbles were 113 nm wide in NB water P. However, note that because of the detection limit, the size distribution below 100 nm is unreliable. Therefore, the spectra may indicate the tail of the size distribution, which has smaller values than those obtained. The concentration of air bubbles in pristine NB water was evaluated to be  $0.38 \times 10^8$  particles / mL. The experimental error for size and concentration were  $\pm 5$  and 20 %, respectively. After 7 days of storage, the concentration of bubbles was almost the same, i.e.,  $0.56 \times 10^8$  particles / mL, although the large bubbles with diameters of ~200 nm disappear due to dissolution into water. Thus, it can be concluded that air bubbles in NB water remain for at least 7 days.

### *3.2 Removal of radioactive Cs from gravel conglomerates*

As shown in Fig. 2, the removal ratios of Cs-137 by washing using NB water and purified water were 17%, and 2%, respectively. This result indicates that NB water is more effective in the removal of radioactive Cs than purified water. Additionally, the NB water collected after washing was more turbid than the purified water that was collected after washing. In order to clarify the state of Cs after washing, we measured the radiation intensity of the filtered water after washing: It was less than detection limit. Note, the mechanism for the removal of radioactive Cs is still unclear; several possibilities include



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surface adsorption (Stride 2008), surface charge (Takahashi 2005), and bubble nucleation, which acts as an abrading agent (Takahashi et al. 2002). However, we consider that Cs was removed with clay.

The removal performance of NB water after storage for various periods was also examined. The removal ratio of Cs-137 using NB water stored for 7 days was 21%, as shown in Fig. 2. Note that the experimental error was large because sufficient gravel conglomerate could not be obtained for examination. However, it is concluded that NB water maintained its removal performance after storage for 7 days. This advantage is useful for on-site removal of radioactive Cs because NB water can be prepared in advance and transported.

*3.3 On-site removal demonstration of radioactive material at Fukushima using tap water*

We conducted a removal demonstration on gravel conglomerate at Fukushima Prefecture to determine the effectiveness of the process. In this demonstration, the precise composition of radioactive material was unknown because only a Geiger-Mueller survey meter was used. However, the main radioactive components can be safely assumed to be Cs-134 and 137, because other kinds of radioactive nuclei cannot spread far from a nuclear reactor<sup>2</sup>. Therefore, it is expected that the gamma count rate is proportional to the amount of

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Cs-134 and 137. Hereafter, the removal ratio of radioactive material is reported as the ratio of the gamma count rate before washing to that after washing.

Figure 3 shows the maximum value of the concentration of air bubbles in water plotted against the operation time of the centrifugal gas–liquid separation machine using tap water collected at Fukushima. As clearly shown in the figure, the maximum value of the concentration of bubbles increases with the operation time as does the removal ratio of the radioactive material. This result indicates that the removal ratio of Cs increases with the maximum value of the concentration of bubbles in water.

The removal ratio was also examined for pure water, water with detergent, and NB water with detergent, as shown in Fig. 4. We see that NB water is more effective for removing of the radioactive material than purified water, and is comparable to water with neutral detergent. These results indicate that the NB water made of tap water at Fukushima can work well for removal of radioactive materials on asphalt or concrete. Thus, NB water is a potential candidate for cleaning polluted objects.

## Conclusions

We examined the removal performance of NB water for radioactive Cs from various materials. It was found that water containing air bubbles around 100 nm in diameter

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is effective, although the removal mechanism of radioactive Cs is still unclear. Additionally, removal performance is still maintained after storage for 7 days. The on-site removal demonstration at Fukushima revealed that NB water made from tap water can indeed remove radioactive materials from gravel conglomerate and is comparable to water with neutral detergent in terms of removal performance. It was also found that the removal performance depends on the maximum value of the concentration of bubbles in nanobubbled water.

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## Figure and table captions

Table 1 Sample notation and preparation conditions with mode size and total concentration of air bubbles in water. The experimental errors for size and concentration were  $\pm 5$  and 20 %, respectively. Figure 1 Distribution of bubble size in NB water measured using laser-illuminated optical microscopic technique.

Figure 2 Removal ratio of Cs-137 for pre-washed gravel conglomerates using NB water P, 7 d, and purified water.

Figure 3 Relation between the maximum value of the concentration of bubbles in water (■) and removal ratio of Cs (□) from gravel conglomerate plotted against duration for NB water generation.

Figure 4 Removal ratio of Cs-137 plotted against radiation intensity of gravel conglomerate before washing for plain water (■) and NB water (●).

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Table 1 Sample notation and preparation conditions with mode size and total concentration of air bubbles in water. The experimental error for size and concentration were  $\pm 5$  and 20 %, respectively.

Sample notation	Preparation		Storage time	Mode size of bubbles (nm)	Concentration of bubbles in water (mL <sup>-1</sup> )	Removal ratio (%) of Cs-137
	Amount of purified water (L)	Flow rate (L/min)				
NB water	50	45 for water	As pristine	113	$0.38 \times 10^8$	17
		0.7 for air	7 days	105	$0.56 \times 10^8$	21
Purified water	Purified tap water collected at Asahi-machi, Takatsuki, Osaka, Japan			no bubbles	no bubbles	2

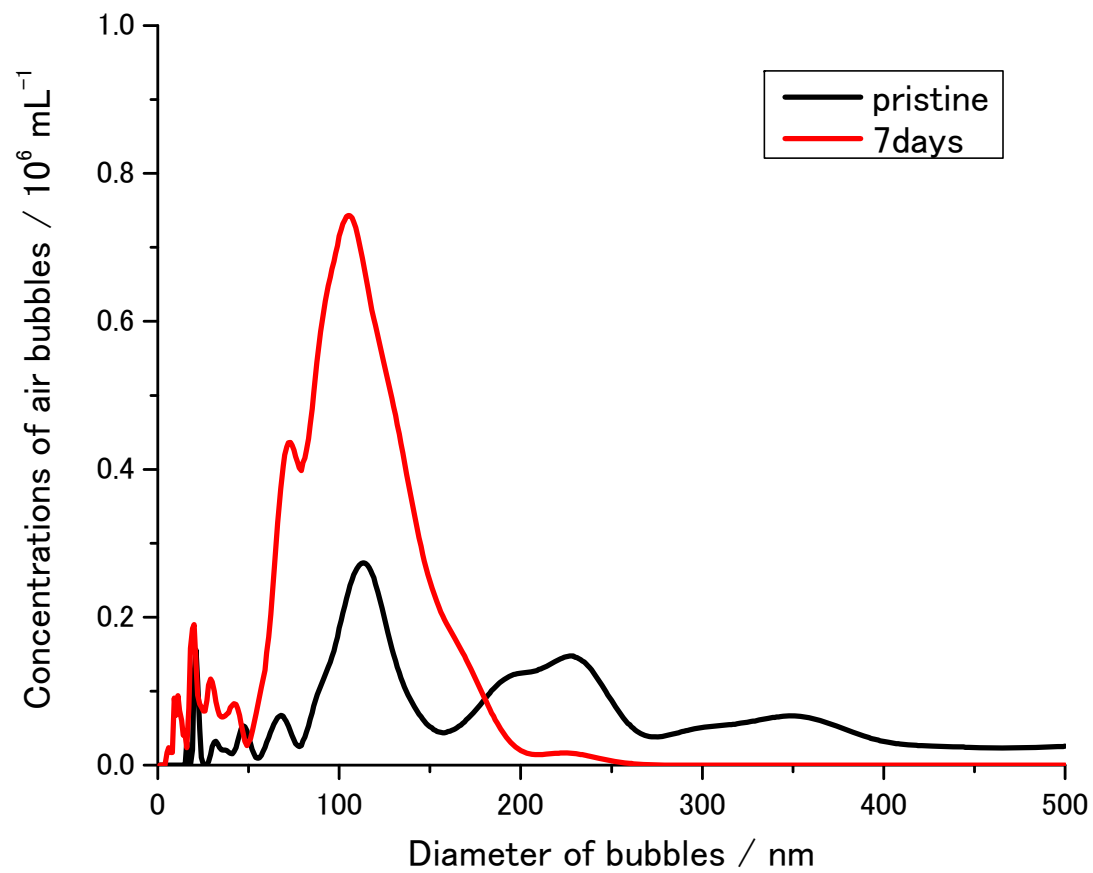


Figure 1 Distribution of bubble size in NB water measured using laser-illuminated optical microscopic technique.

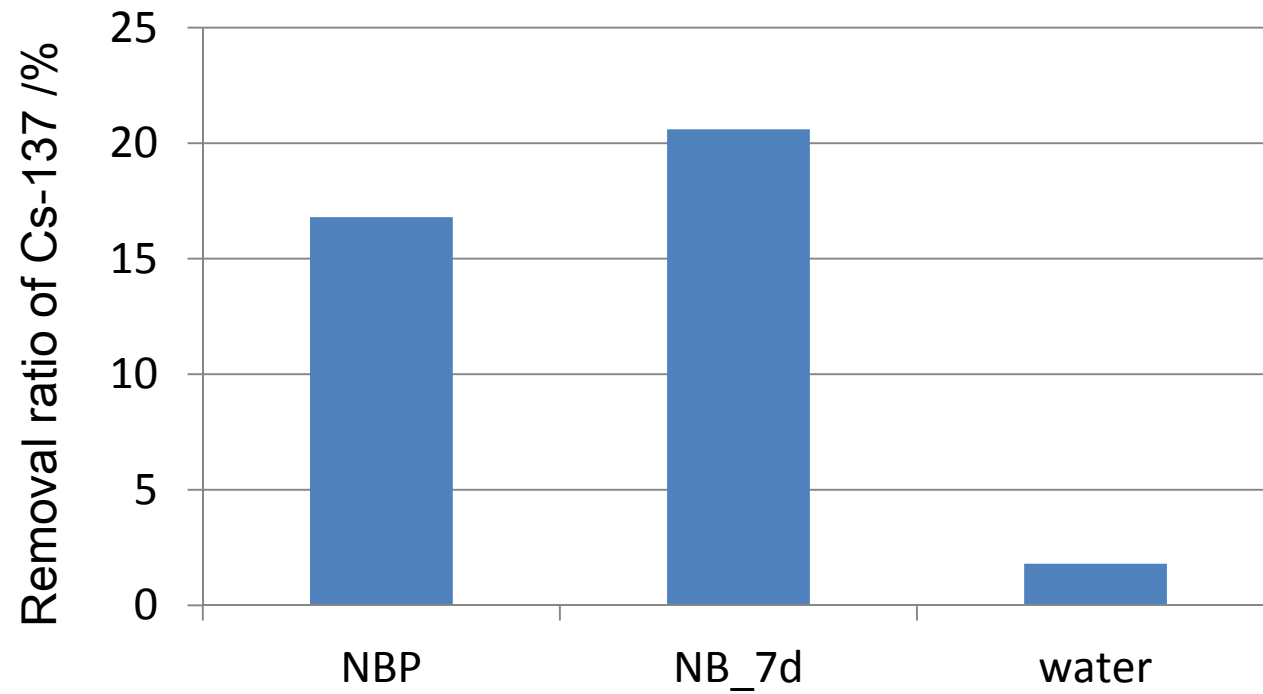


Figure 2 Removal ratio of Cs-137 for pre-washed gravel conglomerates using NB water P, 7 d, and purified water.



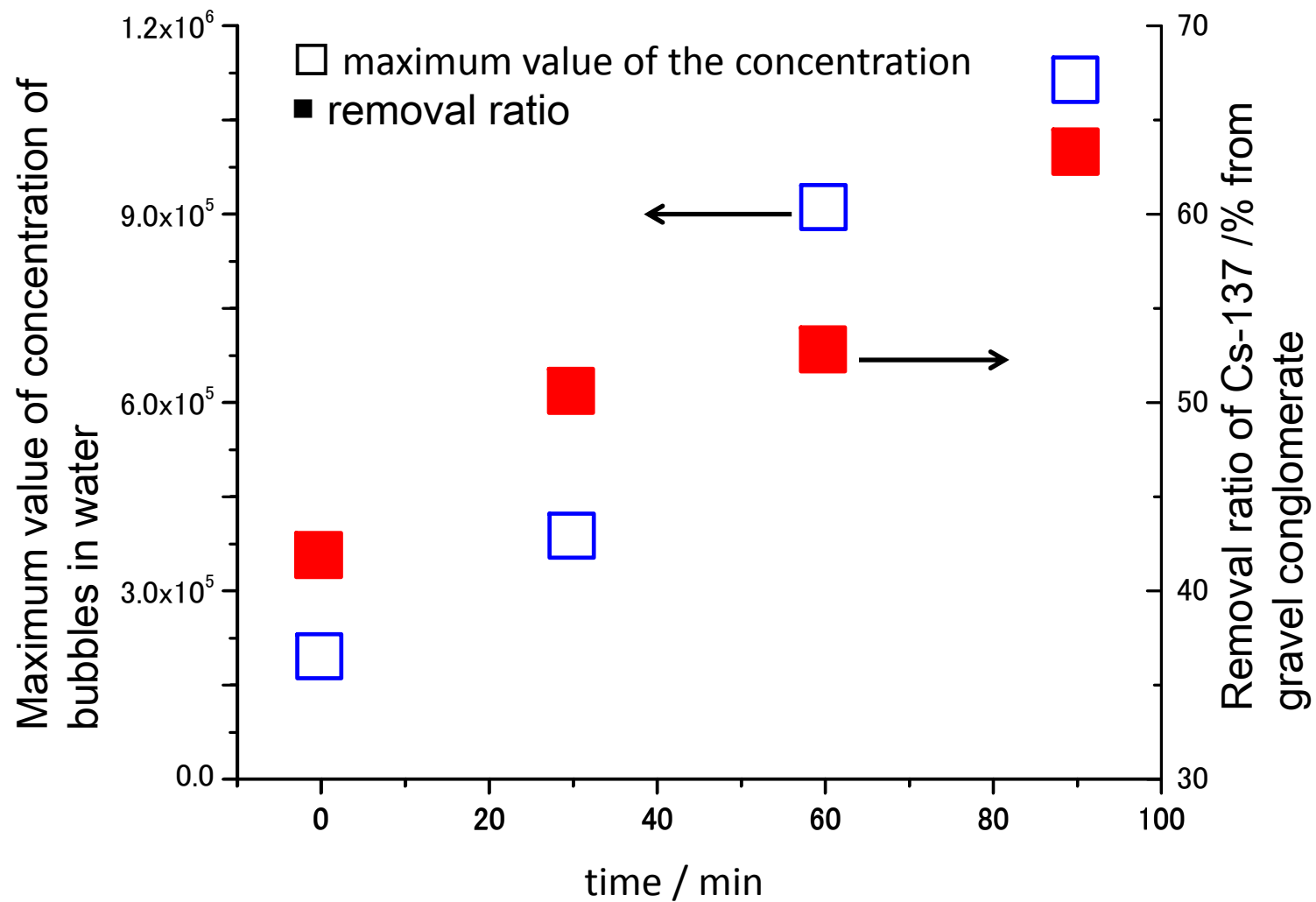


Figure 3 Relation between the maximum value of the concentration of bubbles in water (■) and removal ratio of Cs (□) from gravel conglomerate plotted against duration for NB water generation.

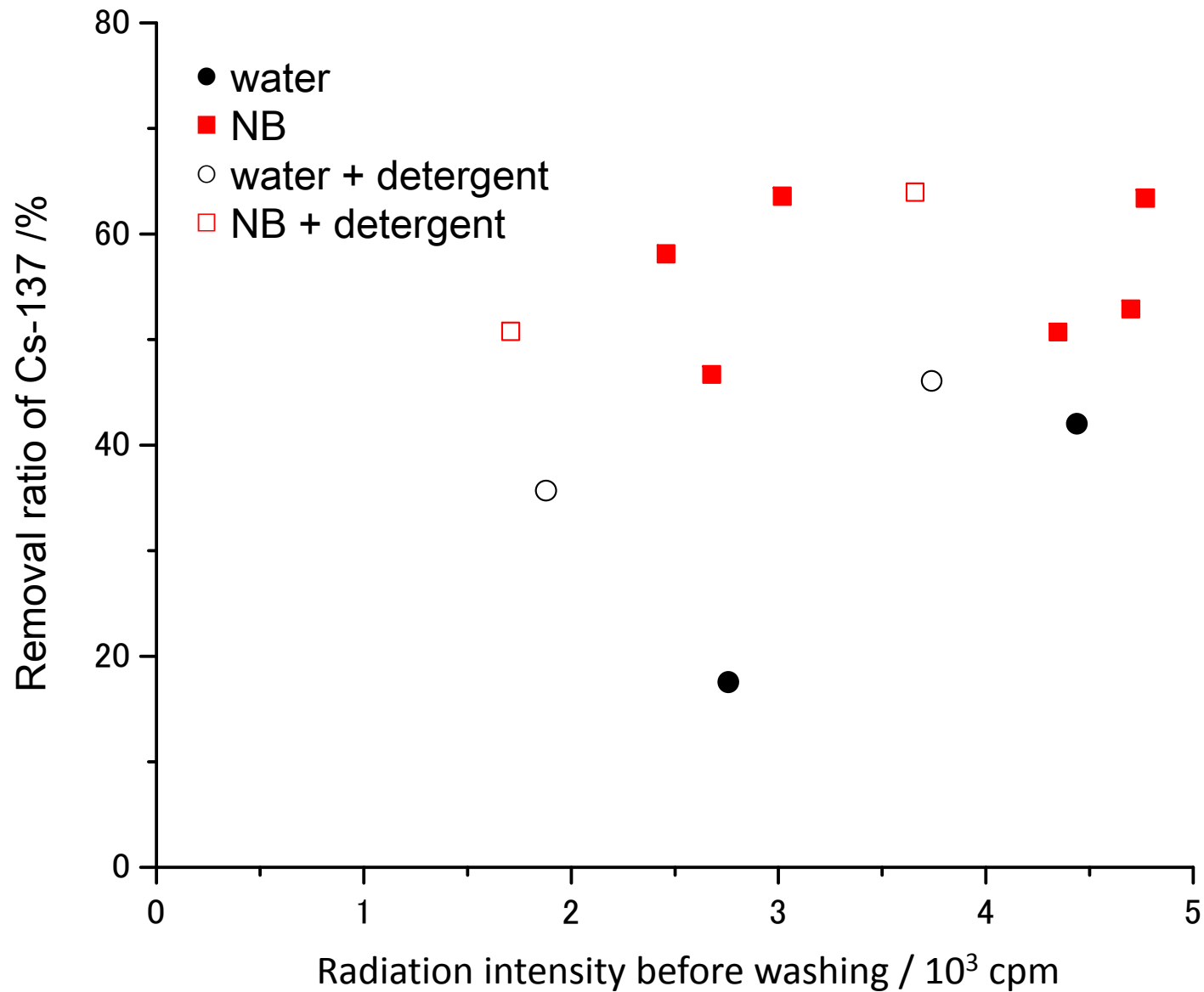


Figure 4 Removal ratio of Cs-137 plotted against radiation intensity of gravel conglomerate before washing for plain water (■) , plain water with neutral detergent (□) , NB water (●), and NB water with neutral detergent (○)